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IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC BATH COMPOSITION FOR INTEGRAL COLOUR ANODISING OF ALUMINIUM AND ITS ALLOYS.

PROVISIONAL SPECIFICATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and ARUMUGAM PALAMALAI, Junior Scientific Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3, India, both Indian citizens.

This invention relates to improvements in or relating to integral colour anodising of aluminium and its alloys.

Hitherto it has been proposed to adopt the following electrolytic processes for integral colour anodising of aluminium and its alloys :

1. Oxalic acid + Sulphuric acid + Inhibitor (Developed in Hungary)
1. Sulphuric acid + an organic acid like oxalic, malonic, lactic or malic acid + a salt of the organic (mainly oxalic acid) and a metal of group IB, VIIB or VIII of the Periodic Table (French Process)
3. Kalcolour, Duranodic and Veroxal processes
4. Autokolor HSH Process (Hungarian).

These processes are open to the objections as described below :

The disadvantage of process (1) is that the depth of the colour cannot be increased beyond a limit. Thus, oxide coatings similar to medium grey films are produced.

In Process (2), rather higher current density in the order of 1.3 to 6.5 A/dm² (the preferable range being 5 to 5.2 A/dm²) should be employed. In order to maintain the current density, specified above, anodisation in this bath consists of a progressive increase of the applied electrical voltage from an initial value of about 20V to as high a value as 250V for some alloys of aluminium. Hence, the bath gets heated steadily, as anodising proceeds. So, cooling is necessary in this bath to a greater extent than in the newly proposed baths where the current density falls off as anodising, proceeds since the bath voltage is kept constant. Only direct current is used in this process.

All the three processes, employ baths containing sulphuric acid (or alkali sulphate), along with aromatic sulphonic acid like sulphosalicylic or sulphophthalic acid and other addition, if any, *e.g.*, maleic acid in Veroxal Process. These baths contain rather higher concentrations of the costly sulphosalicylic acid, for example :

Kalcolour Process	7-15% sulphosalicylic acid
Duranodic Process	10% "
Veroxal Process	5% "
	plus maleic acid

Anodising is not done with AC to attain sufficient depth of colour. A duration of 50-60 minutes is required. In certain cases, it is at least 20-40 minutes.

Even though in Process (4), different shades of yellow, red and brown colours can be obtained, they are not sufficiently deep. We have made improvements over this process. Practically at the same concentrations of chemicals, to get deeper coloured coatings in Process (4), rather higher voltage should be employed as compared to that in the new bath. This point is illustrated in the table in Example 1. Use of higher cell voltage to produce darker coatings is limited in Process (4) by the production of sparks.

The object of this invention is to obviate these disadvantages by changing one or two components of the bath employed in Process (4) (5-sulphosalicylic acid + Formic acid + Hydroquinone).

To these ends, the invention broadly consists in using any one of the organic compounds such as pyrogallol, pyrocatechol, p-aminophenol and metol, in the place of hydroquinone in the above said bath. In the case of baths containing pyrogallol and pyrocatechol, to get deeper coloured coatings, initially we have to anodise a specimen at a relatively higher voltage for at least three to five minutes. This operation is required for a bath only once at the beginning and not for every specimen, anodised in that bath.

Hydroquinone can also be replaced by the cheaper boric acid to get slightly deeper coloured coatings when DC is used and more shining coatings when AC is employed.

More readily available (in our country) tartaric or citric acid can be used in the place of formic acid, only if metol is used instead of hydroquinone to get black coloured anodic coatings.

Most of the compounds employed in the place of hydroquinone, permit the use of comparatively higher bath voltages thus enabling us to produce relatively darker coloured coatings.

The composition of the electrolyte and the anodising conditions are as follows :

Composition

5-Sulphosalicylic acid :	1-10% w/v
Formic acid	1-10% w/v
Pyrogallol, pyrocatechol, p-aminophenol, metol or boric acid	0.3-4% w/v

Anodising conditions

Temperature	30±3°C
Time	20-25 minutes
Bath voltage (AC or DC)	50-130V
Current density :	0.8-4 A dm²
Cathode	Lead

Maximum anodic current density is reached after switching on. But within one or two minutes, it falls to the above specified low value. Thus, voltage or current is to be regulated only during first two minutes. Air agitation and cooling arrangements are required. In AC, initial maximum current density is lower than in the case of DC. Anodic current density falls slowly to average value in the case of AC.

The following typical Examples are given to illustrate the invention :

Example 1

Specimens of 3S aluminium alloy are etched (if necessary), polished (mechanically, or better chemically or electrochemically) and degreased with trichloroethylene. They are then anodised in the following electrolyte :

Composition

5-Sulphosalicylic acid	4% w/v
Formic acid	4% w/v
Pyrogallol	

Anodising conditions

Temperature	30±3°C
Time	20-25 minutes
Bath voltages (AC or DC)	50,60,70 and 80V
Current density	0.8-4 A|dm²
Cathode	Lead

In the beginning, a specimen is anodised at 100V for 5 minutes.

At different bath voltages, anodic coatings of different shades of colours are produced. At each voltage, the colour obtained from this bath is deeper than from the bath employed in the Autokolor HSH Process, practically under the same concentrations of chemicals. This is illustrated in the following Table,

Voltage DC	Colours of anodic coating from baths containing	
	Pyrogallol	Hydroquinone Autokolor HSH Process
50V	Yellowish green	Feeble yellow
60V	Brown	Yellowish green
70V	Chacolate	Light brown
80V	Dark Brown	Brown

Under similar conditions, colour obtained by AC is different from DC. For example, the pyrogallol bath produces at 70V (AC), red brown coating on the 3S alloy instead of the chacolate colour with DC. Employing AC in this pyrogallol bath, different tones of red coatings are produced.

In AC also, the coatings from pyrogallol bath are deeper than from hydroquinone bath (same concentrations of chemicals). Same trend is observed when 2S alloy and extruded aluminium like B51 SWP are anodised in the above said bath. 1% pyrogatechol or p-aminophenol can play the same role as pyrogallol. Added to this, they permit anodising at even 90V without spark production.

Example 2

5-Sulphosalicylic acid :	4% w|v
Formic acid :	4% w|v
Metol :	1% w|v

Anodising conditions: as given in Example 1.

In this bath, different shades of blackish brown coatings are formed on 3S alloy and even at 120V, there is no spark production. But being a darker colour, there is no appreciable distinction in the shades of coatings at different voltages.

Example 3

3S alloys is anodised in the following bath under the same anodising conditions as in Example 1.

5-Sulphosalicylic acid :	4% w|v
Formic acid :	4% w|v
Boric acid :	2% w|v

In this bath, slightly deeper coloured coatings are produced under identical voltages as compared to the bath of the Autokolor HSH Process when DC is used. In AC, the anodic films are of lighter but of more shining colours.

Example 4

3S alloy is anodised in the following electrolyte :

5-Sulphosalicylic acid:	4% w|v
Tartaric or citric acid:	4% w|v
Metol:	1% w|v

Anodising conditions are as in Example 1.

Greyish black coatings are obtained. Distinction in colour at different voltages is not much. Even up to 110V, there is no spark production.

In this bath, instead of metol, either hydroquinone or pyrogallol or pyrocatechol produces only very light gray coloured anodic films.

Example 5

Double Anodising

3S alloy is first anodised in 15% sulphuric acid solution at 2° C under a current density of 12 as for 30 minutes. It is then anodised in the pyrogallol bah (Example 1) at 80 and 90 volts at the same temperature for 20 minutes.

This improves the quality of finish. The coatings are more smooth and shining.

The following are among the main advantages of the invention :

1. Even baths containing cheaper or more readily accessible (in our country) chemicals such as boric acid, tartaric acid and citric acid could produce deeper coloured coatings.
2. Since AC can also be used, the production is high in AC because at both poles, anodising takes place. AC produces different tones of red colours. All these bring down the cost of production of even darker coloured coatings.
3. Modifications of the bath permit higher bath voltages thereby allowing the production of darker coloured anodic films.
4. Only 4% of the costly sulphosalicylic acid is used.
5. Current density is relatively lower (0.8-4 A\|dm²) and current is to be regulated only during first two minutes.
6. Since anodising is carried out at constant bath voltage the current density falls off as anodising proceeds.
7. Relatively shorter time of anodising (20-25 minutes) is employed. Yet, the films are capable of withstanding wear, tear and corrosion.
8. Different bath voltages give different coloured coatings. Colour obtained by AC is different from DC under the same conditions. Thus, choice of colours is wider.

R. BHASKAR PAI

Patents Officer.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Dated this 5th day of August 1971.

COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, Delhi-1, India, an Indian Registered Body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and ARUMUGAM PALAMALAI, Junior Scientific Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3, India, both Indian citizens.

This invention relates to an electrolytic process for integral colour anodising of aluminium and its alloys.

Hitherto it has been proposed to adopt the following electrolyte|processes for integral colour anodising of aluminium and its alloys:

1. Oxalic acid + sulphuric acid + Inhibitor (Developed in Hungary)
2. Sulphuric acid + an organic acid like oxalic, malonic, lactic or malic acid + a salt of the organic (mainly oxalic acid) and a metal of group IB, VIIB or VIII of the Periodic Table (French Process)
3. Kalcolour, Duranodic and Veroxal Processes
4. 5-Sulphosalicylic acid + Formic acid + Hydroquinone (Autokolor HSH Process)

These processes are open to the objections as described below:

The disadvantage of Process (1) is that the depth of the colour cannot be increased beyond a limit. Thus, oxide coatings similar to medium gray films are produced.

In Process (2), rather higher current density in the order of 1.3 to 6.5 A/dm² (the preferable range being 5 to 5.2 A/dm²) should be employed. In order to maintain the current density specified above, anodisation in this bath consists of a progressive increase of the applied electrical voltage from an initial value of about 20V to as high a value as 250V for some alloys of aluminium. Hence, the bath gets heated steadily as anodising proceeds. So, cooling is necessary in this bath to a considerable extent.

All the three processes, employ baths containing sulphuric acid (or alkali sulphate) along with aromatic sulphonic acid like sulphosalicylic or sulphophthalic acid and other addition, if any, *e.g.*, maleic acid in Veroxal process. These baths contain rather higher concentrations of the costly sulphosalicylic acid, for example:

Kalcolour Process	7-15% sulphosalicylic acid
Duranodic Process	10% sulphosalicylic acid
Veroxal Process	5% sulphosalicylic acid *plus* maleic acid

Anodising is not done with AC to attain sufficient depth of colour. A duration of 50-60 minutes is required. In certain cases, it is at least 20-40 minutes.

Even though in Process (4), different shades of yellow, red and brown colours can be obtained, they are not sufficiently deep. We have made improvements over this process. Practically at the same concentrations of chemicals, to get deeper coloured coatings in Process(4), rather higher voltage should be employed as compared to that in the new bath. This point is illustrated in the table in Example 1. Use of higher cell voltage to produce darker and thicker coatings is limited in Process(4) by the production of sparks. Thus, only 40-80V can be employed here.

The object of the present invention is to obviate these disadvantages by modifying the Process 4 for integral colour anodising of aluminium and its alloys, wherein 5-sulphosalicylic acid (1-8%), formic acid (1-8%) and hydroquinone (0.5-2%) are used (Autokolor HSH Process, Hungarian) at 40-100 volts AC or DC. According to the present invention, there is provided an electrolytic process for integral colour anodisation of aluminium and its alloys comprising use of a bath containing 1-7% w/v sulphosalicylic acid 1-10% w/v of a low molecular weight organic aliphatic acid such as formic, tartaric or citric acid and 0.3 to 4% w/v of addition agents like pyrogallol or pyrocatechol or p-aminophenol or metol, or boric acid and the rest being water.

A combination of 1-10% w/v tartaric acid or citric acid and 0.3 to 4% w/v of metol is used to give black anodic coatings. Anodizing is carried out at a constant voltage range from 50 to 130V for a period of 20 to 25 minutes at 30±3°C.

The invented process involves the use of a lower percentage of 5-sulphosalicylic acid compared to the process known earlier. It is also discovered that organic compounds such as pyrogallol, pyrocatechol, p-aminophenol and metol gives deeper shades when used instead of hydroquinone in the bath. In the case of bath containing pyrogallol and pyrocatechol to get deeper coloured coatings, initially the aluminium alloy specimen should be anodised at a relatively higher voltage for at least three to five minutes. The operation is required for a bath only once at the beginning and not for every specimen anodised in that bath.

Hydroquinone can also be replaced by the cheaper boric acid to get slightly deeper coloured coatings when DC is used and more shining coatings when AC is employed.

Tartaric acid or citric acid when used in the place of formic acid and metol is used instead of hydroquinone gives a black coloured anodic coatings on aluminium and its alloys. All the above-described compounds employed in the bath in place of hydroquinone permit the use of comparatively higher bath voltages thus enabling to produce relatively darker and thicker coatings.

The composition of the electrolyte and the anodising conditions are as follows:

5-sulphosalicylic acid	1-7% w/v
Formic, tartaric or citric acid	1-10% w/v
Pyrogallol, pyrocatechol, p-aminophenol, metol or boric acid	0.3-4% w/v
Rest being water	

Anodising conditions

Temperature	30±3°C
Time	20-25 minutes
Bath voltage (AC or DC)	50-130V
Current density	0.8-4 A/dm²
Cathode	Lead

Maximum anodic current density is reached after switching on. But within one or two minutes, it falls to the above specified low value. Thus, voltage or current is to be regulated only during first two minutes. Air agitation and cooling arrangements are required. In AC, initial maximum current density is lower than in the case of DC. Anodic current density falls slowly to average value in the case of AC.

The following typical Examples are given to illustrate the invention:

Example 1

Specimens of 3S aluminium alloy are etched (if necessary), polished (mechanically or better chemically or electrochemically) and degreased with trichlorethylene. They are then anodised in the following electrolyte.

Composition

5-sulphosalicylic acid	4% w/v
Formic acid	4% w/v
Pyrogallol	1% w/v
Anodising conditions	
Temperature	30±3°C
Time	20-25 minutes
Bath voltages (AC or DC)	50,60,70 and 80V
Current density	0.8-4 A/dm²
Cathode	Lead

In the beginning, a specimen is anodised at 100 V for five minutes.

At different bath voltages, anodic coatings of different shades of colours are produced. At each voltage, the colour obtained from this bath is deeper than from the bath employed in the Autokolor HSH Process, practically under the same concentrations of chemicals. This is illustrated in the following Table:

Voltage DC	Colours of anodic coating from baths containing	
	Pyrogallol	Hydroquinone (Autokolor HSH Process)
50V	Yellowish green	Feeble yellow
60V	Brown	Yellowish green
70V	Chocolate	Light brown
80V	Dark Brown	Brown

Under similar conditions, colour obtained by AC is different from DC. For example, the pyrogallol bath produces at 70V(AC) red brown coating on the 3S alloy instead of the chocolate colour with DC. Employing AC in this pyrogallol bath, different tones of red coatings are produced.

In AC also, the coatings from pyrogallol bath are deeper than from hydroquinone bath (same concentrations of chemicals). Same trend is observed when 2S alloy and extruded aluminium like B51 SWP are anodised in the above said bath. 1% pyrogallol or p-aminophenol can play the same role as pyrogallol. Added to this, they permit anodising at even 90V without spark production.

Example 2

5-sulphosalicylic acid	4% w|v
Formic acid	4% w|v
Metol	1% w|v
Rest water	

Anodising conditions as given in Ex. 1.

In this bath, different shades of blackish brown coatings are formed on 3S alloy and even at 120V, there is no spark production. But being a darker colour, there is no appreciable distinction in the shades of coatings at different voltages.

Example 3

3S alloy is anodised in the following bath under the same anodising conditions as in Example 1:

5-sulphosalicylic acid	4% w|v
Formic acid	4% w|v
Boric acid	2% w|v
Rest water	

In this bath, slightly deeper coloured coatings are produced under identical voltages as compared to the bath of the Autokolor HSH Process when DC is used.

Example 4

3S alloy is anodised in the following electrolyte:

5-sulphosalicylic acid	4% w|v
Tartaric or citric acid	4% w|v
Metol	1% w|v

Anodising conditions are as in Example 1.

Greyish black coatings are obtained. Distinction in colour at different voltages is not much. Even upto 110V, there is no spark production.

In this bath, instead of metol, either hydroquinone or pyrogallol or pyrocatechol produces only very light grey coloured anodic films.

Example 5

Double anodising

3S alloy is first anodised in 15% sulphuric acid solution at 20°C under a current density of 12 asf for 30 minutes. It is then anodised in the pyrogallol bath (Example 1) at 80 and 90 volts at the same temperature for 20 minutes. This improves the quality of finish. The coatings are more smooth and shining.

The following are among the main advantages of the invention:

1. Anodic coating of a particular shade is produced in the new baths at relatively lower bath voltage (10-20V less) and hence at lower electrical power consumption. Thus, electrical power consumption is reduced to some 75-85% under identical concentrations of chemicals in the electrolyte.

2. Certain formulations of the new baths permit higher bath voltages thereby allowing the production of still darker and thicker anodic films (as may be required sometimes) even on commercially pure aluminium and simple alloys like 2S and 3S.

3. One formulation of the new baths employs cheaper boric acid in twice the amount as hydroquinone. Yet, the electrolyte is cheaper than the bath containing hydroquinone as the cost of hydroquinone is about 2.5 times that of boric acid.

We claim:

1. An electrolytic process for integral colour anodizing of aluminium and its alloys comprising the use of a bath containing 3-7% w/v sulpho salicylic acid, 1-10% w|v of a low molecular weight aliphatic acid such as formic, tartaric or citric acid and 0.3 to 4% w|v of addition agents like pyrogallol or pyrocatechol or p-aminophenol or metol or boric acid and the rest being water.

2. The process as claimed in (1) wherein a combination of 1-10% w|v tartaric acid or citric acid and 0.3 to 4% w|v metol is used to give black coloured anodic coatings.

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Dated this 26th day of June 1972.

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